Synchrotron Infrared Microspectroscopic Studies of the Changes of the Chemistry of Ink

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INTRODUCTION

Major components of inks have molecules that are vibrationally active and thus give infrared spectra. These components are related to both the type of ink involved, and they are part of a total system, along with possible metal ion-based molecules, that make up the chemistry of inks. In this proposed study, modern synchrotron radiation-based---as well as conventional---infrared spectroscopy will be used to provide a better chemical signature of the composition of inks with respect to their vibrationally-active organic constituents. Results from the proposed work here are important for an effective technique for dating the age of an ink on a document.

The hypothesis of the proposed research is that the aging profile of the drying of an ink can be followed by measuring both gross and subtle changes in the vibrational spectra of the ink's components. The vibrational spectra of organic molecules present in the ink, for example, can be monitored and studied using extremely sensitive analytical and spectroscopic techniques such as synchrotron-based Fourier transform infrared (SR-FTIR) spectromicroscopy. In the case of naturally occurring organic molecules, for example, synchrotron-based FT infrared spectromicroscopy techniques have been used [Holman et al, J. Microbiological Methods, 34, 59(1998)] to map the organic compounds as a function of biological stress in their host microbes.

The use of this technique has been well established for other systems with organic compounds. Analyses of spatially resolved SR-FTIR spectra have been previously used to study the chemistry of organic molecules involving the organic components of microorganisms. The organic compounds in these systems were shown to exist as a function of their surface location and the chemistry they underwent. Both the time- and space-resolved SR-FTIR spectra gave valuable information regarding the organic-related processes involving the microbes. With this effort, the use of SR-FTIR for providing chemical information about organic compounds and their reactions was demonstrated. This method can now be expanded to examine the aging of inks with respect to organic constituents and processes of dehydration that are too subtle for routine instrumental analysis to detect and adequately measure.

Designing effective strategies for understanding the amount and vibrational states of organic molecules and their role in an ink and its chemical changes requires an accurate characterization and fundamental understanding of the nature and molecular form of the organic molecules and their chemistry as the chemistry changes. The surface/bulk chemistry of an ink can be highly variable at the microscopic level, which arises on a small-scale (ranging from a micron to hundreds of microns) microscopically. The methodology commonly used to study this phenomenon is that of combined microscopic imaging and spectromicroscopy techniques, such as infrared microscopy described herein. This approach can also be included with, for example, synchrotron radiation-based x-ray fluorescence spectromicroscopy that can also detect possible metal ions such as iron in the ink, metal ions whose elemental distribution and profile may change as a function of the differing chemistry of the ink. Synchrotron-based x-ray fluorescence

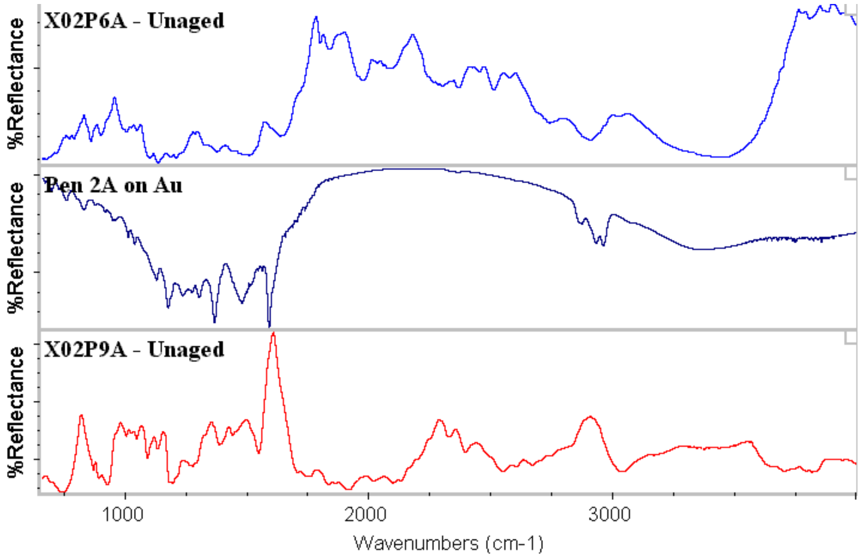

Fig. 1. Infrared spectra of a) a commercial blue ink on a commercial business paper, Xerox 4200DP, b) a commercial black ink on a reflecting metallic substrate, and c) a commercial red ink on the same Xerox 4200DP paper. The background base spectrum of the paper in the spectrum of each ink has been subtracted.

microprobe techniques have been used [Perry et al, Appl. Spectrosc., 51, 1781(1997)] to map transition metal ions such as iron, and it should be a highly effective complement to infrared spectroscopy currently used in the present application here.

The present research involves SR-FTIR spectromicroscopy study the organic molecular profiles of inks in order to determine unique characteristic vibrational profiles as a function of both different inks and their chemical changes. The amount of the vibrationally-active molecules and their chemistry in the inks with respect to one another have been studied over time using the above-mentioned techniques. Figures 1 and 2 show differences in several of the inks as a function of both their inherent chemical differences and their application to various papers. Different techniques such as de-hydration and heating have been used to simulate the process of aging. SR-FTIR spectromicroscopy has been used, because it has been proved to be a sensitive analytical technique capable of providing direct molecular information on organic chemical compositions. The infrared approach can work at spatial resolutions of 10 microns or better.

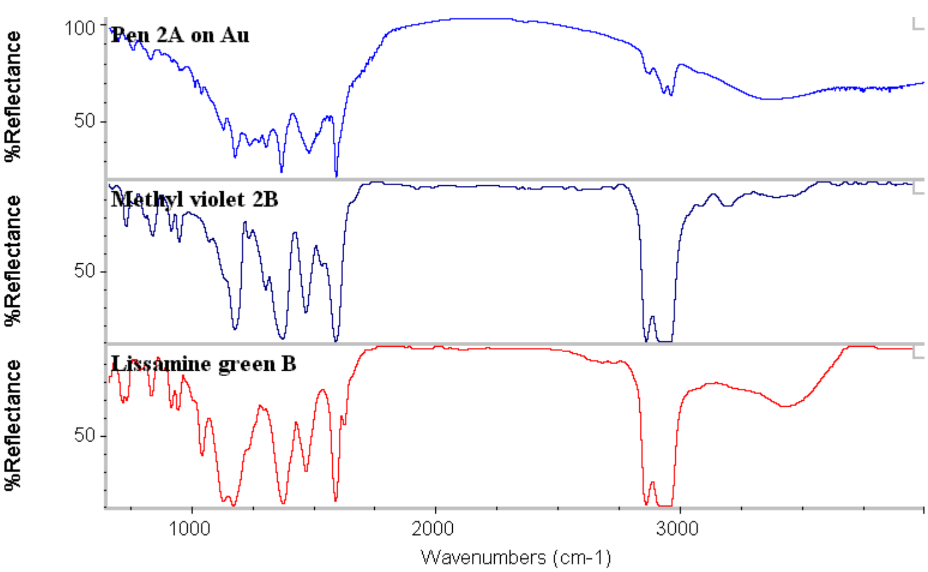

Fig. 2. Infrared spectra of a) a commercial black writing ink on a reflecting metallic substrate, b) a database-derived infrared spectrum of methyl violet 2B, and c) lissamine green B.

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